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Investigation of Bromonitrocamphane

INVESTIGATION OF BROMONITROCAMPHANE

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY PAUL CURTIS GWINN

ENTITLED INVESTIGATION OF BROMONITROCAMPHAUE

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

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Final Examination*

*Required for doctor's degree but not for master's

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History 1001: Introduction to Canadian History

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Investigation of Bromo Nitro Camphane.

Purpose:

The object of this investigation was to obtain additional evidence of the structure of bromo nitro camphane.

Historical:

The series of compounds which formed the subject of the present investigation were studied by M. O. Foster some years ago.

Bromo nitro camphane is formed in a quantitative yield by treating camphor oxime at zero degrees with potassium hypobromite according to the following equation:

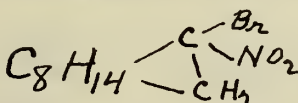


It is a very indifferent compound and can be distilled from an aqueous solution potassium hydroxide without decomposition. On reduction with zinc and acetic acid, camphor oxime and campholenitrile are obtained. This indicates that the bromine and nitrogen are combined to the same carbon atom. The compound does not decolorize potassium permanganate. It is slowly soluble in hot concentrated nitric acid, from which solution it can be precipitated, without any apparent change, by diluting with water. It gives Lieberman's test for nitroso compounds and is optically active. It dissolves readily in concentrated sulphuric acid at zero degrees, giving a small yield of a compound, $\text{C}_{10}\text{H}_{14}\text{ONBr}$, and tarry decomposition products. This new compound is not optically active. Foster called the compound, $\text{C}_{10}\text{H}_{15}\text{O}_2\text{NBr}$, a bromo nitroso

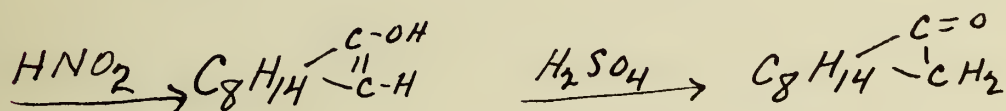
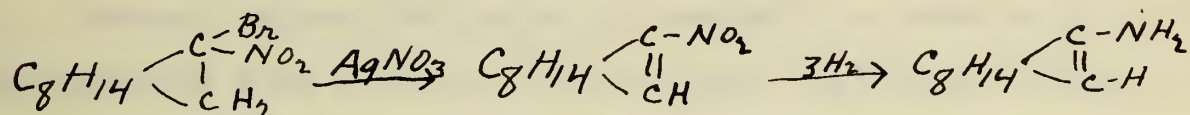
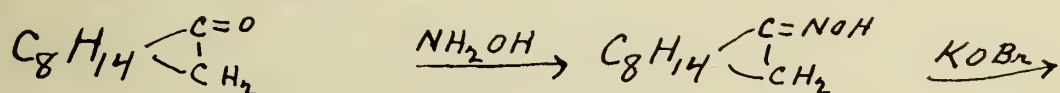
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derivative of camphor oxime in his first paper (T.J.O.C. 75, 1141).

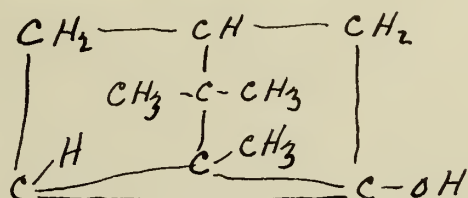
In a later paper (T.J.O.C. 79, 646) Foster treated the compound $C_{10}H_{16}O_2NBr$ with an excess of silver nitrate in absolute alcohol. From the results of his study he assigned the following

structure C_8H_{14}  to the compound and

called it bromo nitro camphane. Foster reported the following compounds and some of their derivatives:



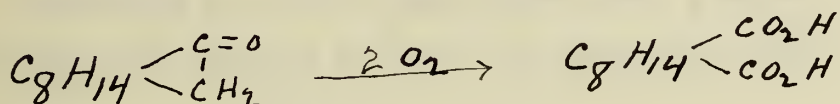
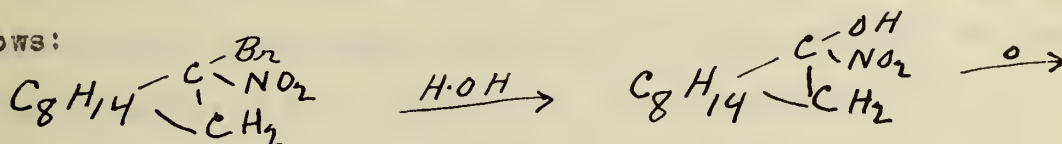
In a still later article, Foster reported the investigation of hydroxy camphene (T.J.O.C. 81, 264). This compound added one atom of bromine, giving a compound which gave camphor on reduction and α campholenic acid on hydrolysis. This structure was then assigned to hydroxy camphene.



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If $C_8H_{14} \begin{array}{l} \diagup C \begin{array}{l} \text{Br} \\ \text{NO}_2 \end{array} \\ | \\ CH_2 \end{array}$ is the correct structure of bromo nitro-

camphane, one would expect to obtain camphoric acid by oxidation with dilute nitric acid. The reaction could be expressed as follows:



However, no positive tests for camphoric or camphoronic acid were obtained from a number of nitric acid oxidations carried out under varied conditions.

Experimental

Bromo nitro camphane was oxidized in two ways, namely, with dilute nitric acid, and with the dilute nitric acid solution containing the theoretical quantity of silver nitrate to remove all the bromine in the compound as silver bromide.

Oxidation by nitric acid alone was studied first. This oxidation was carried out on the steam bath for seventy-two hours in an acetylation flask.

The bromo nitro camphane dissolved slowly in the hot nitric acid, sp. gr. 1.26. It is volatile on the steam bath and each time an oxidation was carried out, some of the unchanged bromo nitro camphane sublimed into the neck of the flask.

The oxidation products may be roughly divided into two parts: ^{or} the greater portion/which is in solution in the clear, brown nitric acid solution, and a small quantity of a heavy, dark brown, viscous oil which separated out at the bottom of the flask. The latter oil is very resistant to oxidation. It was warmed on the steam bath with dilute nitric acid for three weeks without any apparent change. At the end of that time, it was subjected to steam distillation, when a light yellow, sticky and viscous oil distilled over. An analysis of this oil showed nitrogen and bromine to be present. It decomposed a little sodium bicarbonate but the major part of it was non acidic.

The nitric acid solution was decanted from the oily residue mentioned above, and evaporated to dryness on the steam bath,

leaving a light yellow residue. This was neutralized with ammonium hydroxide, filtered and barium chloride added to the filtrate which was then warmed. No insoluble barium salt precipitated from the solution which showed camphoronic acid to be absent. Each successive oxidation residue was treated as described above. Several times a slight cloudiness was noticeable on adding the barium chloride, but no better tests were obtained.

In another oxidation the clear nitric acid solution was diluted with water and extracted with ether, the ether solution being washed with water to free it of nitric acid as far as possible. On evaporation of the ether, a light yellow, viscous, and fragrant oil was obtained. An elementary analysis on this oil showed nitrogen and bromine to be present in considerable quantity. The oil decomposed calcium carbonate rapidly, precipitating at the same time a dark brown viscous oil which failed to dissolve on the addition of an excess of calcium carbonate. This oil was removed by extracting the solution with ether. The clear solution of the calcium salt was then concentrated in a vacuum desiccator. In a few hours a dark brown oil rose to the surface of the solution and the solution became acidic towards litmus. This acidity could not be removed by adding an excess of calcium carbonate, so the solution was extracted with ether to remove the oil and the clear solution neutralized with lime water. On further concentration of the aqueous solution, more oil separated and the solution again became acidic. The solution was treated as described above. The same treatment was repeated several times more, but the calcium

salt finally obtained contained the oil as an impurity. It was noticed that calcium bromide was formed when the oil obtained by extracting the clear nitric/^{acid}solution with ether was warmed on the steam bath with an excess of calcium carbonate.

A clear aqueous solution of the calcium salt gave a slight oily emulsion when acidified with hydrochloric acid. Silver nitrate gave a bulky white precipitate but it was contaminated with silver bromide. No satisfactory separation of the products formed by the nitric acid oxidation were obtained.

Oxidation with Nitric Acid and Silver Nitrate.

In the oxidation with nitric acid and silver nitrate, the bromo nitro camphane was treated with the theoretical quantity of silver nitrate to remove all the bromine as silver bromide. The oxidation was carried out on the steam bath for a period of time varying from five hours to five days, with and without an excess of the theoretical amount of silver nitrate.

This reaction was carried out in dilute nitric acid, sp. gr. 1.26, in an acetylation flask. The solution was warmed on the steam bath under varied conditions. In the beginning, the solution was left on the steam bath for five days. Later the period of oxidation was reduced to fifteen hours. The precipitated silver bromide was then filtered off, the acid solution diluted with water and extracted with ether. The weight of the dried silver bromide checked within 0.5 gram of the theory. It was

later found that the silver bromide precipitate contained an indifferent organic substance which was not the original compound and was insoluble in strong sodium hydroxide and organic solvents. The ethereal solution gave a fragrant yellow oil on evaporation which weighed about forty percent. of the original substance used in the reaction (after drying over anhydrous sodium sulphate). This oil was subjected to vacuum distillation. A small yield of a light yellow, indifferent substance, with a fragrant odor distilled over around 230° at 20 mm. pressure. It was recrystallized from petroleum ether twice. After the first recrystallization, it melted 162-4°. Subsequent recrystallizations lowered its melting point until it melted over the range between 120-160°. A qualitative analysis showed it to contain nitrogen but no bromine. This substance was at first thought to be the lactone of cis camphonolic acid reported by Noyes and Tavean (Amer. Chem. Journal 35, 386), M. P. 164-5°. It was warmed for eight hours on the water bath with standard potassium hydroxide from which solution, glistening long crystals separated on cooling, M. P. 178-9°.

The same fragrant white indifferent substance was obtained along with impurities in small yields, each time the compound $C_{10}H_{16}NO_2Br$ was oxidized with silver nitrate and dilute nitric acid. It is insoluble in water and soluble in the usual organic solvents. Many attempts were made to separate the indifferent substance into one or more compounds but none were very satisfactory. However, indications were obtained to show it contained camphor, the unchanged bromo nitro camphane and other compounds.

This indifferent substance was obtained in two other ways, namely,

1. The oily acid, mixed with the indifferent substance, obtained by extracting the nitric acid solution with ether, after filtering off the silver bromide, was neutralized with an excess of sodium carbonate solution, the solution then extracted with ether and the indifferent substance obtained on evaporation of the ether.

2. By steam distillation of the nitric acid solution containing the precipitated silver bromide. The latter method gave the largest yeilds but probably contained more of the unchanged bromo nitro camphane than that obtained by the other methods. The indifferent substance is formed in a small quantity at the beginning of the oxidation. From 25 grams of bromo nitro camphane oxidized under the same conditions the following results were obtained:

15 hour oxidation silver nitrate and nitric acid

1.5 grams

27 hour oxidation silver nitrate and nitric acid

1.6 grams

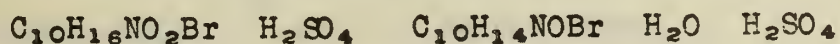
54 hour oxidation silver nitrate and nitric acid

2.0 grams

A sodium fusion on each of the above showed nitrogen and traces of bromine. The M. P. of each was around 160-170°.

The attempt was made to recrystallize the indifferent substance, obtained by steam distillation of the nitric acid solution in five percent. potassium hydroxide solution. The solution was

warmed on the steam bath for eight hours when the hot solution had a strong camphor odor but none of the white solid dissolved. The solid which failed to dissolve was recrystallized from alcohol giving white flakes which had a strong camphor odor and became wax-like when pressure was applied to them. M. P. 160°. A mixed M. P. with camphor was taken. M. P. 155-160°. M. P. of camphor used in the mixed M.P. was 172-174°. Nothing precipitated out of the potassium hydroxide solution on cooling, so it was extracted with ether, yielding a trifling white deposit. The potassium hydroxide solution was then acidified with hydrochloric acid and extracted with ether, yielding a few drops of a viscous brown oil. A portion of the indifferent mixture was dissolved in cold concentrated sulphuric acid and precipitated in a few minutes by diluting the acid solution with water. This yielded a light brown substance which melted at two distinct temperatures, around 174° and around 200° after recrystallization from alcohol. This mixture was treated with cold concentrated nitric acid. The compound $C_{10}H_{14}NOBr$ dissolved in the nitric acid while about half of it did not. The portion insoluble in the nitric acid was a white waxy substance, M. P. 188-190°. A sodium fusion on the latter showed nitrogen to be present. The odor of camphor was not perceptible in this substance but it was readily noticeable before treatment with the sulphuric acid. The reactions are as follows:



The compound $C_{10}H_{14}NOBr$ is soluble in nitric acid in the cold.

That portion of the oxidation products which did not distill in the current of steam was obtained as an impure silver salt on evaporation of the nitric acid solution. The free oily acid was obtained by adding an excess of hydrochloric acid, filtering off the silver chloride and concentrating the solution on the water bath. The attempt was made to obtain a pure silver salt by recrystallization in boiling water, but it was not obtained pure in this way. The silver salt does not all dissolve in nitric acid so probably further oxidation took place while the clear nitric acid solution was evaporated on the water bath, splitting out silver bromide. That portion insoluble in nitric acid dissolves slowly in ammonia. A fragrant brown viscous oil was obtained by extracting the acid solution with ether. This oil was freed of a non-acidic substance by treatment with sodium carbonate which precipitated a sticky brown oil. A little asbestos freed the solution of this brown oil and the sodium salt was boiled with charcoal until it had a light yellow color.

The copper salt of the oily acid was formed as a bright green sticky precipitate on adding dissolved copper sulfate to a solution of its sodium salt, which ^{had been} slightly acidified with acetic acid. This salt is sparingly soluble in water and readily soluble in mineral acids.

An analysis of the copper salt gave :

I		
Weight sample14745	grams
Weight copper oxide....	.04015	" = 21.77% copper
Weight water.....	.0795	" = 5.86% hydrogen
Weight carbon dioxide,,	.205	" = 38.00% carbon

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A second analysis of the same copper salt gave:

Weight sample.....	.19065	grams	
Weight copper oxide...	.04165	"	= 21.85% copper
Weight of water.....	.0795	"	= 6.35% hydrogen
Weight of carbon dioxide	.2738	"	= 39.10% carbon

These analyses give a formula corresponding to $C_{10}H_{18}O_6Cu$ for the first one and $C_{10}H_{18}O_6Cu$ for the second. This showed the substance to be a mixture of acids. To separate the mixture of acids, the copper salt was dissolved in a slight excess of hydrochloric acid, the acid solution being then extracted with ether as long as the ether extract gave a residue. The acidified solution of the copper salt was then treated with a slight excess of the theoretical quantity of sodium acetate to neutralize the hydrochloric acid present. On standing several days, a fine dark green copper salt precipitated from the solution. These copper salts are being further investigated.

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Summary

Bromo nitro camphane was oxidized with dilute nitric acid but no definite compounds resulting from this oxidation were isolated. When bromo nitro camphane was oxidized with dilute nitric acid containing silver nitrate, a mixture of indifferent compounds and the copper salts of a mixture of oily acids were obtained. The best results were obtained from a fifteen hour period of oxidation although the oxidation was carried out for as long a period as seven days.

ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to Professor W. A. Noyes, who proposed this problem, for his assistance and interest during the investigation.

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